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THE EFFECT OF STEAM AS A COMBUSTION RETARDING AGENT
IN THE GASIFICATION OF CRUDE OIL BY PARTIAL COMBUSTION.

by

Harry Adam Grine.

A

T H E S I S

submitted to the faculty of the
SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI
in partial fulfillment of the work required for the

D E G R E E O F
METALLURGICAL ENGINEER

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Professor of Metallurgy and Ore Dressing.

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Investigations of the effect of steam used as a combustion retarding agent to prevent the formation of free carbon, or lamp black by-product in the gasification of crude oil by partial combustion to make producer gas.

One of the most difficult problems in the development of processes and generators for converting the low grade crude oils into producer gas for use in internal combustion engines, has been to prevent the formation of excessive amounts of tar and free carbon or lamp black as a by-product.

These products, under certain conditions, result from the dissociation of the hydrocarbons of which the crude oil is formed. They have, owing to their tendency to accumulate in the gas generators and gas pipes, been the chief cause of all the failures of machines designed to make producer gas from the low grade crude oils. These oils are cheap in price and used almost exclusively in portions of the United States for the production of power.

Previous to these investigations the production of tar and free carbon by-product have been generally accepted as unavoidable results in the gasification of crude oils by direct partial-combustion processes. Various means have been devised for overcoming the difficulties which these by-products cause where continuous operation and production of gas is required.

In one of the machines which has been commercialized a holder capacity is provided which permits of a sufficient storage of gas to operate the engines during short burning-out periods. In this way the carbon accumulations within the generator are burned out.

In another apparatus or system duplicate units are

provided so that one generator can be kept in operation while the other is being cleaned. From an engineering standpoint such machines are makeshifts and require considerable attention and labor to contend with a product which should not be formed.

In a generator which I designed for gasifying the low-grade asphaltum base crude oils of Southern California, these carbon deposits are accumulated in a bed of coke where they are held in a permeable state on the surface of the coke until gasified by slow partial combustion.

In the development of this generator, I found that these carbon deposits became excessive and necessitated occasional applications of a poke bar to the coke bed to keep it in a thoroughly permeable state. I therefore decided to make an investigation of the partial combustion of the crude oil, which took place above the coke bed, in order to develop if possible a method of controlling the amount of free carbon deposited from the crude oil, by controlling the rate of combustion.

These investigations extended over a period of more than a year and were conducted on a 50 horse power unit Grine Oil Gas Producer. A number of tests were conducted with various forms of atomizing nozzles, methods of introducing the air for combustion, variations of the proportions of oil and air and operation under pressure and ^{with} vacuum on the generator. The greater part of these tests attempting to accomplish re-

sults in a mechanical way were very disappointing and accomplished nothing towards solving the problem. These tests will not be discussed and only those which had to do with the final solution of the problem by the use of steam will be described.

The theoretical assumptions on which the tests with steam as a combustion retarding agent were based are as follows:-

1. If the ignition of the mixture of oil and air for combustion could be retarded in the combustion chamber above the fuel bed, until the crude oil had become sufficiently hot to flash and disseminate, by reason of its rapid expansive property, throughout the air for combustion, an intimacy of contact between the fuel and air would be secured, superior to any which could possibly be secured by mechanical means.

2. That when this condition of dissemination and intimate contact of fuel and air was secured a homogeneous combustion would result and destructive distillation and its consequent formation of free carbon by-product would be eliminated.

Previous experience had practically proven that the free carbon by-product resulted from destructive distillation and decomposition of part of the crude oil before it had been brought into contact with air for combustion.

The crude oils used in these investigations were low grade asphaltum base California crude oils. These oils have a specific gravity of 12° Baume' to 20° Baume'. An ultimate analysis shows on a 14.5° Baume' oil:-

Carbon ----- 87.64

Hydrogen ----- 10.48

Sulphur -----	1.02
Oxygen -----	.08
Nitrogen -----	.78

The gas generating system consisted of a generator, water tower scrubber and gas cooler, steam boiler, positive pressure air blower, rotary gear oil pump, and a centrifugal water circulating pump for circulating the water used in scrubbing and cooling the gas. The water flowed from the overflow pipe of the tower scrubber to a sump and was returned from there to the top of the scrubber by the circulating pump.

The generator consisted of a vertical^{al}, cylindrical steel-shell 5½ feet in diameter and 8 feet in height. It was lined with refractory clay lining 9 inches thick giving an inside diameter of 4 feet. In the top was a 10 inch diameter opening with a removable cover plate. This opening was used when starting up to charge coke into the generator and as a stack opening while heating up the generator. Near the bottom and situated on the side of the shell was a gas outlet-nozzle and opposite to it a clean-out door. Just above the gas outlet-nozzle was a grate of refractory-clay bars which spanned the generator and formed a support for the bed of coke.

Near the top and located on the side of the shell was a saddle flange into the inner side of which was screwed a 3" standard pipe which extended through the lining and formed a passage for the air supplied for combustion. This 3" pipe had a long thread which extended through the saddle flange and re-

ceived a 3" standard Tee. The oil atomizer entered this tee in the back end of the run and was directed horizontally into the air delivery pipe with the tip just slightly beyond the inside of the lining.

The air delivery pipe connecting the positive blower with the generator entered the 3" tee in the side outlet. In this air line was a low pressure relief valve and a standard 3" service cock for controlling the air supply.

The arrangement of these parts is shown in the attached drawings which show a vertical cross section through the center of the generator and a front elevation.

The oil was pumped from a storage tank by a rotary gear-pump and delivered to a pressure supply-tank. This tank was connected to the crude-oil atomizer on the generator by a 3/8" pipe in which was located a globe valve for controlling the supply of oil to the atomizer. The pressure on the oil system was regulated to 35 pounds gauge by installing a relief valve in a return flow pipe leading from the pressure supply tank back to the storage tanks.

The pop valve on the steam boiler supplying steam to the generator was set for 75 pounds gauge pressure. The steam pressure was reduced by means of a Davis Steam Pressure Regulator, to 35 pounds gauge pressure at the atomizer. At the atomizer the steam line was divided into two branches, one leading into the atomizer and one to a connection on the lower side of the 3" tee. Each branch was fitted with a globe valve for controlling the amount of steam.

The process carried out in this apparatus is as follows:-

The crude oil is subjected to partial combustion with air in the combustion chamber above the coke bed. This forms a combustible gas of low heat value which carries in suspension, tarry vapors and free carbon in various quantities, depending upon the operating conditions. The products formed in the upper combustion chamber are forced downward into and through the bed of coke. The coke bed is brought to an incandescent heat before gas making begins.

In passing through the bed of coke the tarry vapors are broken down into light hydrocarbon gases and the free carbon is filtered out and deposited on the surface of the coke where it is retained until gasified by combination with gases which pass into the coke bed incompletely carbonized.

After passing through the coke bed the gases accumulate in the chamber below the grate and pass from there through the gas outlet nozzle to the water tower scrubbing and cooling apparatus. In this scrubber and cooler any by-product which has escaped from the generator is washed out and the gas is cooled.

The indicators by which proper conditions were determined in the tests, were partly chemical and partly physical. In practical work they are entirely physical and the operator judges the working conditions entirely by the observance of the appearance of the fire in the combustion chamber above the fuel bed, by the appearance of a small test flame which is continually burned and by examination of the amount and nature of the by-product being washed out in the scrubber.

For observing the condition of the fire in the combustion chamber above the coke fuel bed, a glass covered peek hole

is provided on a level with and somewhat to the right of the atomizer. Through this, the interior of the combustion furnace can be observed at all times.

In the tests to determine the effect of using steam to control the combustion observations of temperature and gas analyses were made. In order to make clear the action of steam when used to retard the combustion of the oil, it is necessary to describe briefly the ordinary methods of burning crude oil. In practically all combustion furnaces using crude oil as a fuel, a small portion of the air for combustion or steam is used for atomizing the crude oil so as to bring it into contact with the air for combustion. Various forms of atomizers have been devised, all of which are designed to deliver to the combustion furnace on which they are used, a mixture of crude oil and air, or steam in a more or less finely divided state. A further supply of air for combustion is introduced around the atomizer or through air openings situated below the atomizer. In the ordinary method of combustion the rich mixture of crude oil and air ignites at the atomizer forming a long yellow hydrocarbon flame. In such cases there exists a core consisting of a rich mixture of crude oil and air surrounded by an atmosphere of excess air but not in intimate mixture with this air. The deficiency of oxygen within this core to properly unite with the elements of the hydrocarbons of the oil, causes a decomposition of the crude oil and a splitting off of light hydrocarbon gases and the formation of free carbon from which the hydrogen has been split off. This carbon does not ignite readily in the presence

of incoming light hydrocarbons and remains as a by-product residue.

In these investigations the flame condition at the atomizer and its effect on the by-product production were closely observed. It was found to be a very reliable indicator in the adjustment of the steam supply.

Part of the steam used in the tests was used in atomizer of my design. This atomizing steam supply was not varied as the load was practically constant giving an almost constant oil supply. The steam used in controlling the combustion was introduced into the air pipe surrounding the atomizer, through an auxiliary steam supply pipe and valve. The effect of introducing the auxiliary steam into the air was to saturate it before it came into contact with the mixture of crude oil and steam delivered from the atomizer.

The amount of oil used was measured by calibrating the storage tank in inches and fractions of an inch and determining the weight of oil for each division.

The steam consumption was measured in pounds of water evaporated in the auxiliary boiler. All the steam generated was used in the producer and the fire was adjusted so as to prevent popping off on the boiler.

The amount of steam was varied from that used only to atomize the crude oil up to three times by weight, the amount of crude oil being used. In order to allow conditions to become settled on each test the various proportions of oil and steam were maintained as near as possible for a period of two hours. The effect of each increase in steam supply was noted in its effect on :-

1. The condition of the fire in the combustion chamber above the fuel bed of coke.

2. The appearance of the test flame.

3. The amount and nature of the by-product coming from the water tower scrubber.

4. Constituents of the gas.

A number of preliminary tests were run in which no attention was given to recording results. These were to get a general idea of handling the steam supply.

Before beginning the tests, the generator was heated up to approximately 1400°F. During this heating up period, the gases escaped part of the time through the 10 inch opening in the top of the generator. After the combustion chamber had been brought to a dull cherry red, heat the topcover was closed and the waste gases passed through the coke bed for a short period to heat it up. After passing through the coke bed, the waste gases escaped through a purge pipe on the connection between the generator and scrubber.

After the generator had been heated, the stack or purge pipe valve was closed and the air and oil supply adjusted for making an etenuant fuel or producer gas and this gas was passed through the scrubber.

TEST #1.

Oil consumption -----	11.5 gals. per hr.
	or
(Weight per gallon 7.86 pounds)	90.39 pounds.

Water evaporated on boiler -----	70 pounds per hour
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Ratio of oil to water was approximately, Oil : Water :: 9 : 7

The amount of steam supplied in this test was no more than what is ordinarily used in atomizing the crude oil and the auxiliary steam

valve was entirely closed. With these proportions the interior of the combustion chamber was badly clouded with lamp-black or free carbon and only occasional glimpses of the flame at the atomizer could be seen.

The test flame showed considerable red color due to the free carbon carried in suspension in the gas. The scrubber discharge water showed an excessive amount of free carbon. This carbon however, was very fluffy and dry and when rubbed in the hand, showed no tendency to stick and could easily be washed off. This carbon separated from the water and floated on the top of the water in the sump. An analysis of this gas made in a regulation Hempel gas analysis outfit, showed the following constituents.

	% By Volume.
Carbon Dioxide -----	7.0
Oxygen -----	0.0
Olefiant Gases -----	1.0
Carbon Monoxide -----	14.8
Methane -----	5.1
Hydrogen -----	6.4
Nitrogen by difference -----	65.5

TEST #2.

Oil consumption ----- 11.8 gals. per hr.
or
92.748 lbs. " "

Water evaporated by the boiler ----- 95.25 pounds

The ratio of oil to water was approximately Oil:Water::1:1

The condition of the fire in the combustion chamber above the coke bed appeared slightly improved and at times the flame at the atomizer could be seen distinctly. There was still considerable free

carbon clouding the fires.

The appearance of the test flame changed very little if any. The carbon by-product discharged in the scrubber water was less and of apparently the same consistency. The gas analysis showed very little change in the constituents.

	% By Volume.
Carbon dioxide -----	7.0
Oxygen -----	0.0
Olefiant gases -----	1.0
Carbon monoxide -----	15.0
Methane -----	5.4
Hydrogen -----	7.0
Nitrogen by difference -----	64.6

TEST #3.

Oil consumption -----	11.5 gals. per hour		
	or		
	90.39 pounds	"	"
Water evaporated by the boiler -----	140	"	"
Ratio of oil to water was approximately	Oil : Water :: 1 : 1.5		

On this test the auxiliary steam supply was started. There was a marked change in the appearance of the fire in the combustion chamber above the coke bed. The cloudiness due to floating carbon decreased so that the oil flame was plainly visible at the atomizer. At times the oil flame would cease and then flash up again. The general appearance of the fire indicated a marked decrease in the free carbon formed.

The test flame showed much less red color from carbon and began to have a decided blue color.

The amount of by-product coming from the scrubber was re-

duced to less than half of that in the previous tests. The by-product still appeared to be dry-free carbon or lamp-black, which floated on the surface of the water. The gas analysis showed little change except in carbon dioxide and carbon monoxide and a slight increase in the amount of olefiant gases.

% By Volume.

Carbon dioxide -----	6.8
Oxygen -----	0.0
Clefiant Gases -----	1.2
Carbon Monoxide-----	15.2
Methaine -----	5.4
Hydrogen -----	6.6
Nitrogen by difference -----	65.0

TEST #4.

Oil consumption ----- 11.5 gals. per hour.
or
90.39 pounds " "

Water evaporated by the boiler ----180 " " "

The ratio of oil to water was approximately Oil : Water :: 1 : 2

When this proportion of oil to water was reached the flame at the atomizer ceased entirely and the whole interior of the combustion chamber above the coke bed cleared up so that the walls opposite the peek hole were visible through the contents of the chamber.

This was evidently the critical point and this proportion was maintained until its effect on the by-product could be closely watched.

The test flame became practically free from red color-

ation and was almost a clear blue.

The by-product coming from the scrubber showed only a small penciling on the surface of the water and was reduced almost to nil.

A number of gas analyses were made and averaged. Three appeared to be little difference except in the amount of carbon dioxide and Hydrogen.

	% By Volume.
Carbon dioxide -----	6.2
Oxygen -----	0.2
Olefiant Gases -----	1.0
Carbon Monoxide -----	15.2
Methane -----	5.4
Hydrogen -----	4.6
Nitrogen by difference -----	67.4

A test was then made slightly reducing the steam supply at the auxiliary valve. The mixture of oil and steam at the atomizer immediately began alternately igniting and extinguishing in flashes and whenever the flame was visible, the cloudiness due to lamp black could be noted distinctly. Increasing the steam at the auxiliary supply valve suppressed the flame at the atomizer again with the same clearing results.

TEST #5.

Ratio of oil to water was approximately Oil : Water:: 1 ; 2.5

The interior of the combustion chamber above the coke bed became slightly dull but not cloudy as when the flame at the atomizer was permitted.

Near the end of the test the by-product coming from the scrubber showed a tendency to stick and roll together, **showing** the **presence** of tar. This indicated the use of too much steam and a lowering of the temperature of the coke bed so that the tar would not break down.

TEST #6.

The **ratio** of oil to water was increased to approximately:-

Oil : Water :: 1 : 3.

The interior of the combustion chamber above the coke bed became dull in a short time and considerable tar was discharged from the scrubber.

The test flame showed considerable yellow color, due to olefiant hydrocarbon gases.

This test was discontinued in a short time as it was evident that the generator temperature was too low to gasify the oil.

The results obtained from these tests and subsequent operation in accordance with instructions to operators based on test #4 have proven the correctness of the assumptions on which I instituted the tests and have demonstrated:-

1. That steam can be used to retard the combustion of the mixture of oil and steam until this mixture has been brought into intimate contact with the air for partial combustion of the crude oil to form producer gas.

2. That a homogeneous combustion, secured by such retardation until intimacy of contact between the oil and air for combustion takes place, will produce practically no free carbon by-product.

3. That the critical point at which the steam as a combus-

tion retarding agent is most effective and productive of the best results is a ratio of oil to steam of approximately, one part by weight of oil to two parts by weight of steam.

4. That the physical indication of this critical point is when the flaming of the mixture of crude oil and steam at the atomizer just ceases and a clear, transparent condition of the chamber in which the oil is being gasified maintains.

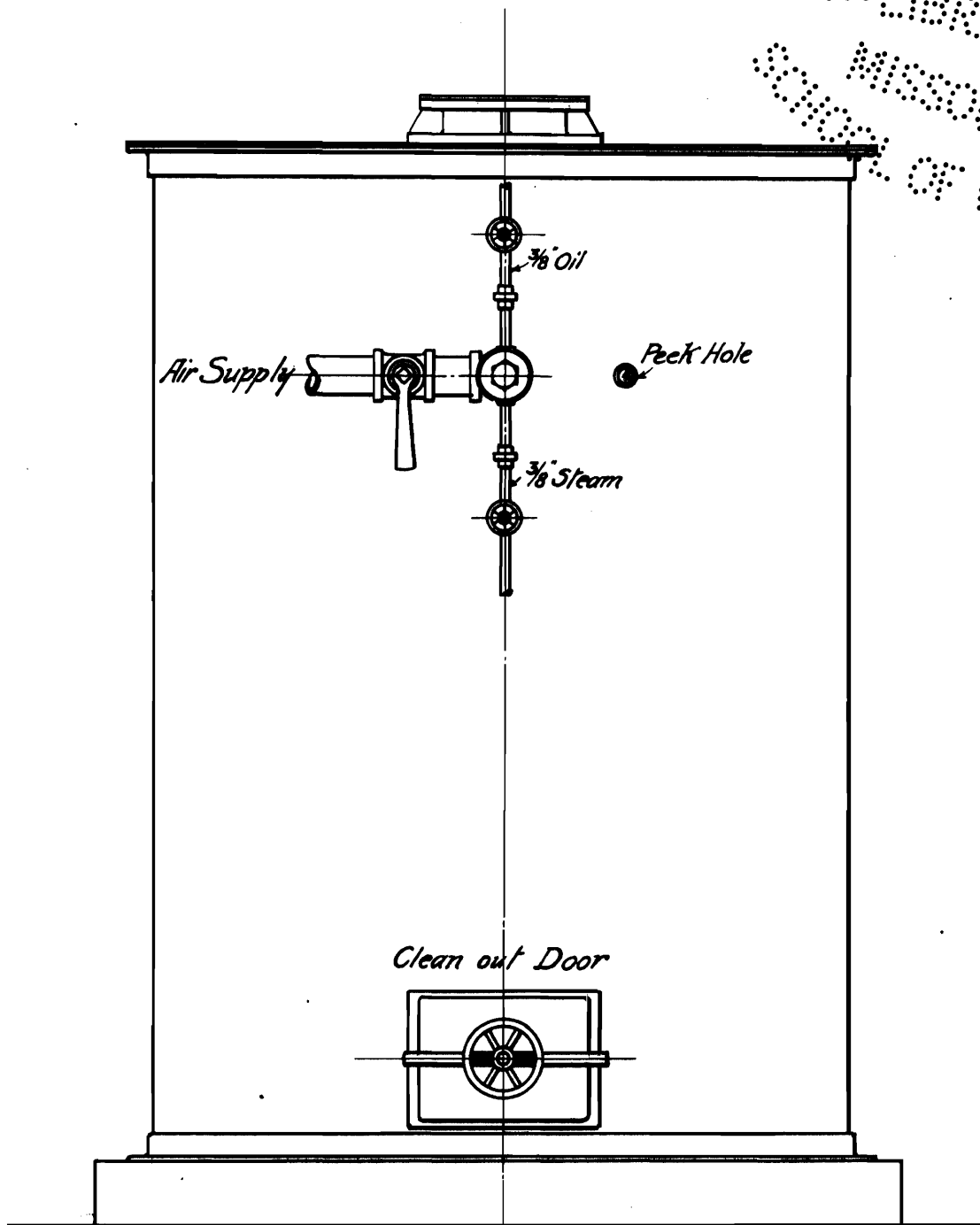
The method of retarding the combustion of crude oil by an auxiliary steam supply to the air for combustion of the crude oil has since these investigations been applied to a commercial plant using the Grine Crude Oil Gas Producer. The unit is operated twenty four hours per day and no cleaning out or poking is necessary.

Practically no by-product is formed and the efficiency is 20 to 25% better than that obtained when free carbon by-product in excessive quantity is formed.

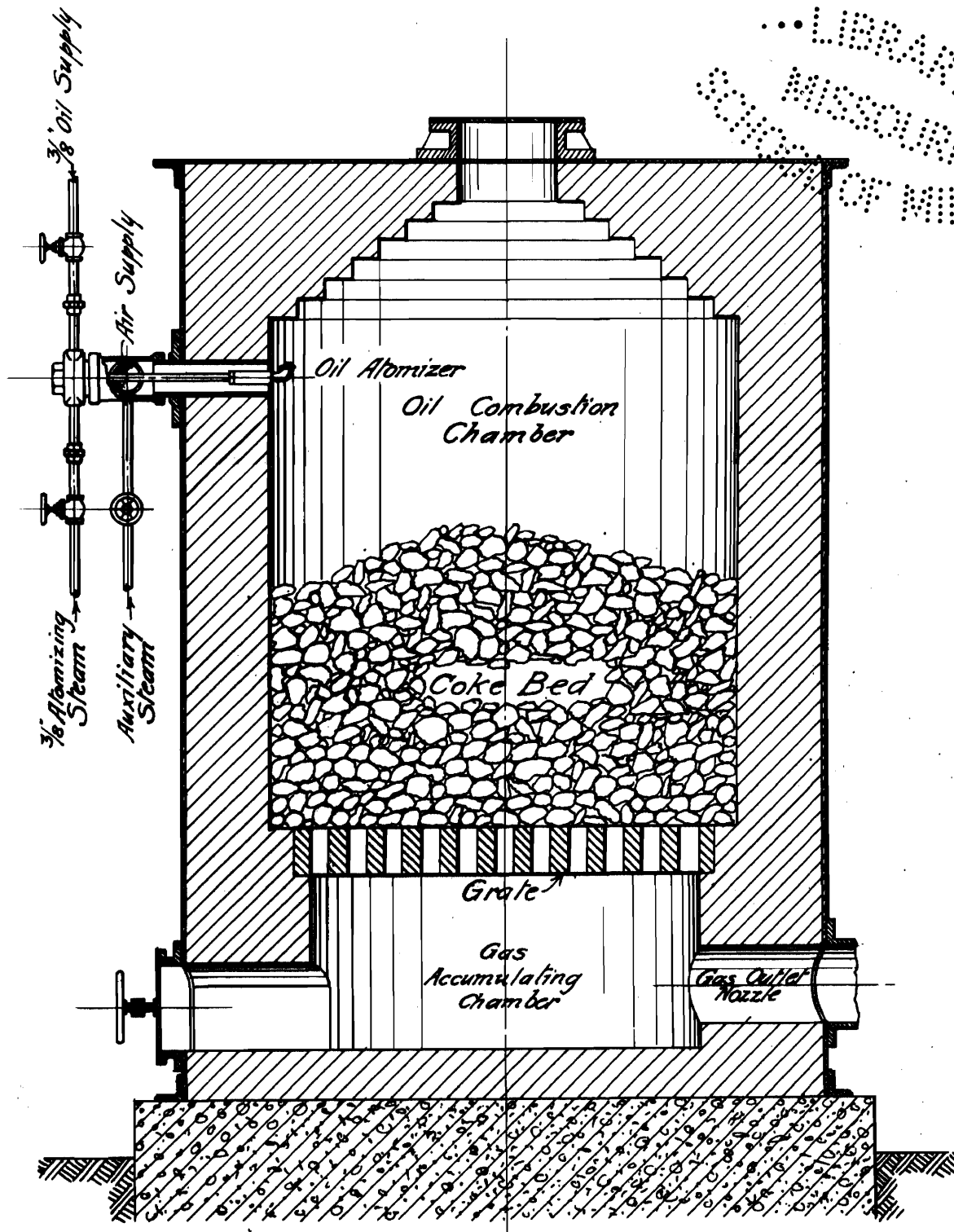
The steam apparently does not enter into the chemical reactions in the generator. A balance of the Hydrogen and Oxygen appearing in a given volume of the gas, and the Hydrogen and Oxygen contained in the crude oil and air used to make the gas shows only the amount of Hydrogen contained in the oil and Oxygen contained in the air.

The temperature, of the mixture is probably maintained below the temperature at which the steam dissociates to any extent into its elements of Hydrogen and Oxygen, and the steam simply acts as a carrier for the crude oil and a temperature deadener until the flashing of the crude oil and its dissemination in intimate mixture with the air takes place.

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